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# Computational study on the electronic transitions of 14-phenyl-14H-dibenzo[a,j]xanthenes

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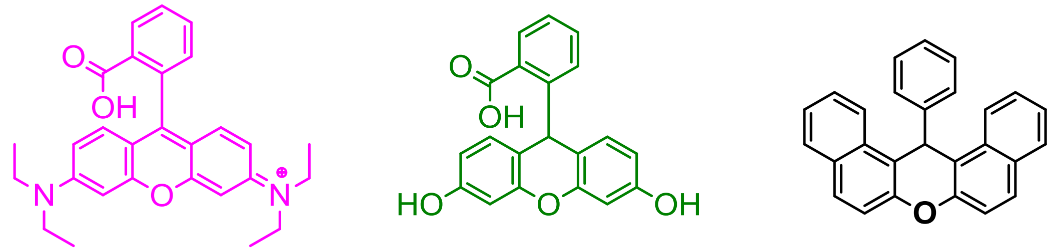
**Abstract :** The present report documents the theoretical study of the electronic transitions in a xanthene derivative, 14-phenyl-14H-dibenzo[a,j]xanthene. The orbitals contributing to the electronic transition are studied. The scope of the work in bring about tailor-made properties has been discussed.

## Introduction

Xanthene derivatives are known to exhibit remarkable biological activities like, antibacterial[1, 2], anti-viral[3] and CCR1 antagonist[4]and enjoys as a motif for the design and development of pharmacological agents[5]. Xanthene derivative serves as very important and useful starting material in the synthesis of compounds with potential material applications. Considering its potentiality, a number of synthetic methodologies have been reported for this core[6,7].

Most of the applications of Xanthene derivatives are mainly due to absorption of energy in the visible range, originating from various electronic transition. Thus, in order to design xanthene based compounds with desired colorimetric or luminescent properties, it is necessary to have an in-depth view of the electronic states and orbitals involved. With this view, the present work reports our findings on the theoretical study of the electronic transitions in a fused-ring xanthene, namely, 14-phenyl-14H-dibenzo[a,j]xanthene (Scheme 1).



Pigment used in pink highlighter

Fluorescein

**14-phenyl-14*H*-dibenzo[*a*,*j*]xanthene**
**(Compound of present Study)**

**Scheme 1**

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The intention behind the choice of the compound, 14-phenyl-14H-dibenzo[a,j]xanthene, for this study is the presence of large conjugated pi-electronic over almost the whole skeletal framework. Hence, understanding of the key-sites bearing commendable control will help an experimental researcher to manipulate the molecular design to emerge out with the desired properties.

### Computational Details

In this work, all the theoretical studies were done using Gaussian03 package. The structure of 14-phenyl-14H-dibenzo[a,j]xanthene was optimized under DFT at B3LYP level of theory with 6-31G** basis set[8,9]. With the optimized structure, the energies and shape of HOMO and first three LUMOs (LUMO, LUMO+1, LUMO+2) were calculated. The electronic transitions were calculated using both HF and TD-DFT.

## Results and Discussions

The broad band observed in the computed electronic spectrum of the compound,14-phenyl-14H-dibenzo[a,j]xanthene, was due to the transition of electrons from a number of closely spaced molecular orbitals. The Density of states (DOS) pattern (plotted with GaussSum package) of the molecular orbitals, taken in the range of -20 to +20 eV energy range (**Figure 1**) indicates a high density of orbitals are present in both the Occupied orbitals and Virtual orbitals regions with a clear demarcation of about 9.66 eV (~270nm).

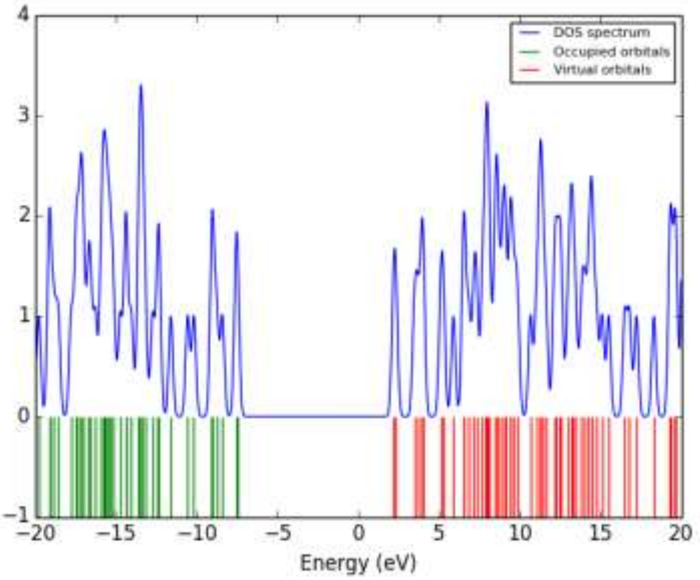

**Figure 1: DOS pattern of the Compound**

The analysis on the contribution of the different orbitals (**Table 1**) shows that, the strongest absorption (Osc Strength = 0.1457) is arising with the transitions HOMO->LUMO (53%) and H-1->L+1 (36%). Though HOMO->LUMO (Transition ‘A’in**Figure** 2) transition is the most significant contributor, the H-1->L+1 transition is also a very prominent one(Transition ‘B’ in **Figure** 2). This closeness in the energy profile can be justified on the basis of the nature of contributing orbitals as shown in **Figure 2**.

**Table 1:** Contribution of the different orbitals in the electronic transition of the compound

| No. | Wavelength (nm) | Osc. Strength | Major contributors | Minor contributors |
|---|---|---|---|---|
| **1** | 269.82 | 0.1457 | H-1->L+1 (36%), HOMO->LUMO (53%) | H-4->L+3 (5%), H-2->L+2 (8%) |
| **2** | 257.34 | 0.0957 | H-1->LUMO (42%), HOMO->L+1 (37%) | H-4->L+2 (6%), H-2->L+1 (4%), H-2->L+3 (7%) |
| **3** | 241.82 | 0.0035 | H-4->LUMO (19%), H-2->L+1 (28%), H-1->L+2 (21%), HOMO->L+1 (12%), HOMO->L+3 (22%) | H-5->LUMO (4%), H-3->LUMO (2%), H-2->L+3 (3%), H-1->LUMO (5%), H-1->L+4 (3%) |

It may be observed (**Figure 2**) that, both the HOMO and H-1 orbitals have very high similarity in terms of the source atom concerned. Both the molecular orbitals are arising from the major contribution of the pi-orbitals of the two naphthalene-framework of the Xanthene. The little energy difference between the two orbitals seems to be due to arise of a node and decrease of contribution the atom Carbon-10

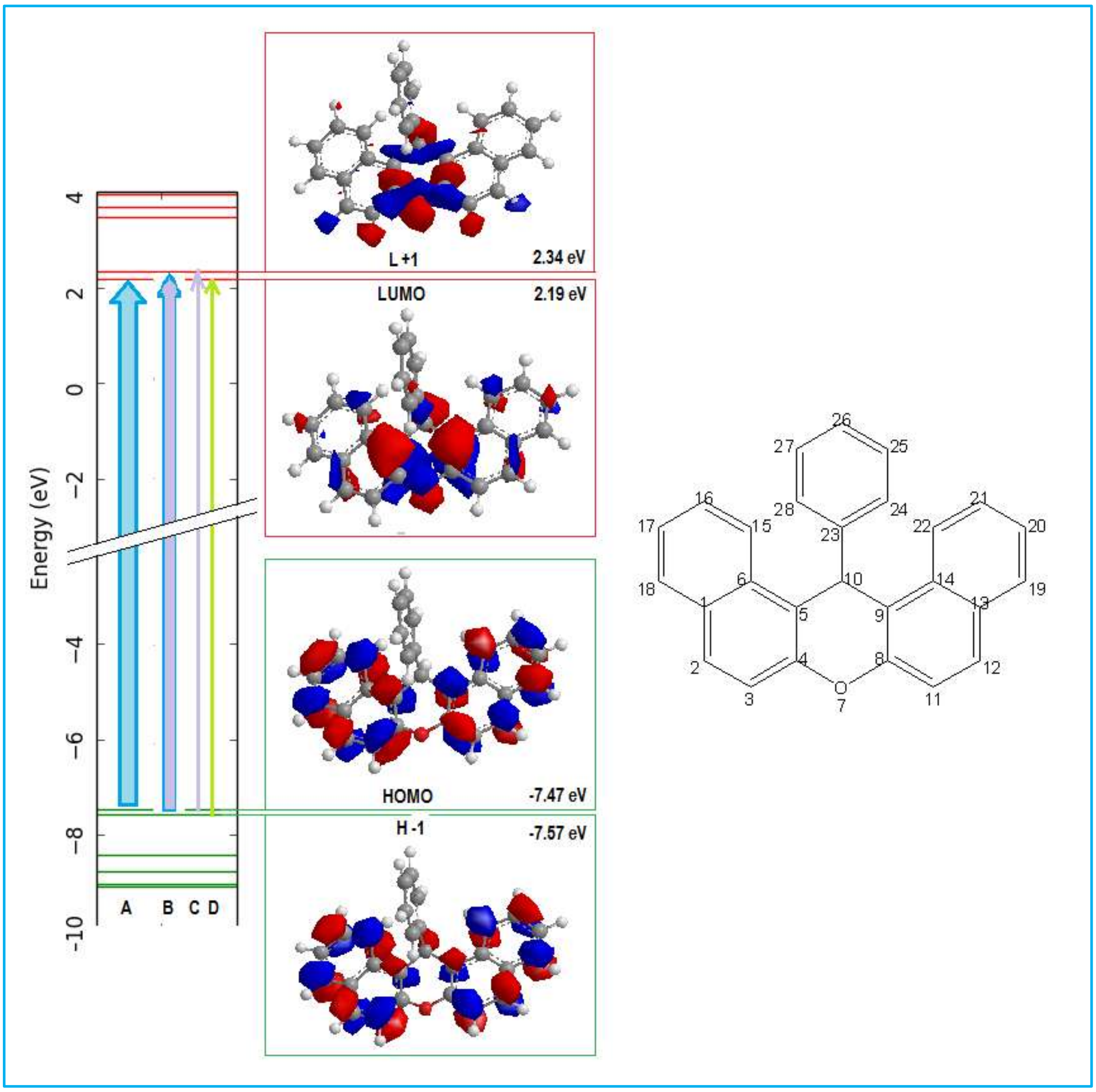

**Figure 2: Major electronic transitions and the contributing orbitals**

On the other hand, the LUMO and L+1 orbitals are mainly arising from the heterocyclic six-member central ring, with the oxygen atom and the Carbon-10 both are sp3 hybridised and hence have lower interaction with the surrounding pi-orbitals, taking them at significantly higher energy compared to that of the HOMO, which mainly arising from the highly conjugated pi-system.

The very closeness of the orbitals HOMO & H-1, and LUMO & L+1 is also responsible for the absorption band at 257.34nm (Osc. Strength = 0.0957). Here the transition is arising mainly due to HOMO->L+1 and H-1->LUMO(Transitions ‘C’ and ‘D’ respectively in **Figure 2**). The third band at 241.82nm is of very low Osc. Strength arising from a number of complicated high energy transitions of low probability.

From the study, it is observed that, in neither of the four major role-playing orbitals, the orbitals of the benzene moiety (connected with Carbon-10) seems to overlap significantly, which seems to be due to the presence of the sp3 hybridised Carbon-10, which breaks the overlapping of the pi-orbitals from the benzene moiety and the rest of the skeleton rendering the structure non-planner.

Thus, introduction of group at the benzene-moiety (connected at Carbon-10) is not expected to bring about considerable change in the HOMO-LUMO energy gap and thereby, in the energy absorption also. On the other hand introduction of electron-donor or electron-withdrawing group at the naphthalene-moiety(is) is expected to bring about significant change in the electronic transition and hence, in the colour profile of the compounds designed with this molecular framework.

## Conclusion

In conclusion, from this computational study of the electronic transitions in, 14-phenyl-14H-dibenzo[a,j]xanthene, the orbitals H-1, HOMO, LUMO and L+1 have been found responsible for the electronic transitions in this framework. For tailoring the electronic transition in compounds designed from this core, introduction of groups at the naphthalene-moiety(is) is expected to bring about significant change in the electronic transition and hence their material properties.

## Acknowledgement

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## References

1. Patil, V. S. *et al.* Synthesis, Characterization, and Antibacterial Activity of Novel (1H-Benzo[d]imidazole-2-yl)-6-(diethylamino)-3H-one-xanthene, Phenoxazine, and Oxazine. *J. Heterocycl. Chem.* 2015, 52:124–129.
2. Singh, H. *et al.* Efficient One Pot Synthesis of Xanthene-Triazole-Quinoline/Phenyl Conjugates and Evaluation of their Antimicrobial Activity. *J. Braz. Chem. Soc.* (2014). doi:10.5935/0103-5053.20140095
3. Reddi Mohan Naidu, K. *et al.* Design, Synthesis and Antiviral Potential of 14-Aryl/Heteroaryl-14H-dibenzo[a,j]xanthenes Using an Efficient Polymer-Supported Catalyst. *Molecules* 2012, 17:7543–7555.
4. Naya, A. *et al.* Design, Synthesis, and Discovery of a Novel CCR1 Antagonist. *J. Med. Chem.* 2001, 44:1429–1435.
5. Goodell, J. R., Puig-Basagoiti, F., Forshey, B. M., Shi, P.-Y. & Ferguson, D. M. Identification of Compounds with Anti-West Nile Virus Activity. *J. Med. Chem.* 2006, 49:2127–2137.
6. Saeed, A., Shabir, G. &Shehzadi, S. A. Synthesis and Characterization of New Xanthene Derivatives, and Their Electrochemical Study. *J. Chinese Chem. Soc.* 2016, 63:181–188.
7. Dabiri, M., Azimi, S. &Bazgir, A. One-pot synthesis of xanthene derivatives under solvent-free conditions. *Chem. Pap.* 2008, 62.
8. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993, 98:5648–5652.
9. Lee, Yang & Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B. Condens. Matter* 1988, 37:785–789.

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